

A Molecular Mechanics Force Field for Rhodium(I) Carbonyl Phosphine Complexes and Its Application on the Oxidative Addition Reactions of These Complexes

DELANIE LAMPRECHT, GERT J. LAMPRECHT

Department of Chemistry, University of the Orange Free State, P.O. Box 339, Bloemfontein 9300, Republic of South Africa

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ABSTRACT: The main purpose of the development of an Rh(I) Carbonyl Phosphine force field was to predict the molecular structure of Rh(I) complexes as well as to compute possible intermediates or transition states during the oxidative addition of CH_3I to these complexes. © 2000 John Wiley & Sons, Inc. *J Comput Chem* 21: 692–703, 2000

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Introduction

Square planar Rh(I) complexes, being coordinatively unsaturated, undergo oxidative addition reactions with various organic and inorganic molecules. Because oxidative addition reactions can proceed via different reaction pathways and because the addition can be either *cis* or *trans*, it is imperative to know the molecular structures of the reactants and products, as well as the nature of

intermediates, to propose suitable reaction mechanisms.

The impetus for these investigations has been the desire to gain a greater understanding of the electronic and steric factors influencing the oxidative addition reactions, which are vital steps in the functioning of many of these compounds in homogeneous catalysis.^{1,2}

Based on kinetic studies,^{3–6} the proposed mechanism of the oxidative addition of CH_3I to Rh(I) Carbonyl Phosphine complexes is a nucleophilic attack by the Rhodium atom on the Carbon atom of the methyl iodide where a linear polar transition state is formed which leads to *trans* addition (Fig. 1).

Correspondence to: D. Lamprecht; e-mail: lamprechd@cem.nw.uovs.ac.za

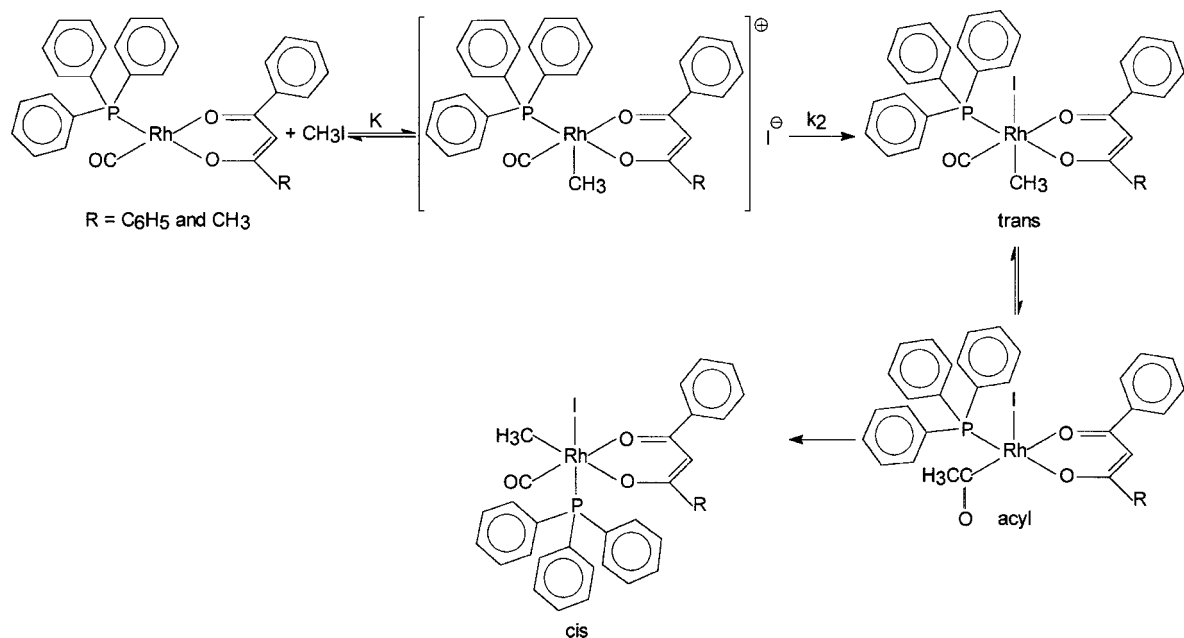


FIGURE 1. Mechanism for the oxidative addition of CH₃I to Rh(I)(1,3-diphenyl-1,3-propanedionato)(CO)(PPh₃).

The possibility of a three-centered polar transition state, which normally leads to *cis* addition, cannot be ruled out⁷ (Fig. 2).

The development of an Rh(I) Carbonyl Phosphine force field, with the aid of molecular mechanics, should offer a better alternative to address the question of intermediates.

The Rhodium(I) Carbonyl Phosphine Force Field

Force fields are developed to treat classes of compounds that are composed of the same atom types. Force fields are usually developed for specific types of molecules, and their use in other situations will either fail or give poor results. Once the appropriate force field has been established, it is used in the minimization of the strain energy of the complex.

One of the most prominent and fascinating features of transition metal complexes is their large variability in molecular geometry, which can be attributed to the electronic structures of the metal

ions possessing partially filled d- and f-orbitals. The ligand sphere and the coordination geometry obviously have a large influence on the kinetic, thermodynamic, and electronic properties of the transition metal. Each structure is a compromise between the demands of the metal ion (mainly electronic effects) and that of the ligand (primarily steric effects). The metal ion demands are rather weak; therefore, models have been proposed that interpret and predict structures of transition metal complexes while completely ignoring electronic effects.

Only a few methods, such as the valence force field method, the point-on-a-sphere method, and the ionic method have evolved to extend an organic force field to treat metal complexes. These methods differ in the type of terms that are added to the potential energy equations to describe the interactions that involve the metal ion.

HyperChem (TM),⁸ a modeling and simulation program of which input is straightforward and computation of the molecular mechanics structures is based on MM⁺, AMBER, BIO⁺, and OPLS methods, was used to run these molecular mechanics calculations.

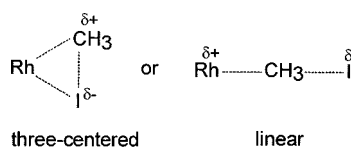


FIGURE 2. The two possible intermediates that can occur during oxidative addition.

THE MM⁺ FORCE FIELD

MM⁺ is derived from Dr. Allinger's MM2 force field,⁹ which was developed in 1977. The MM⁺ force field will perform a calculation with the existing parameters and will, therefore, use default values

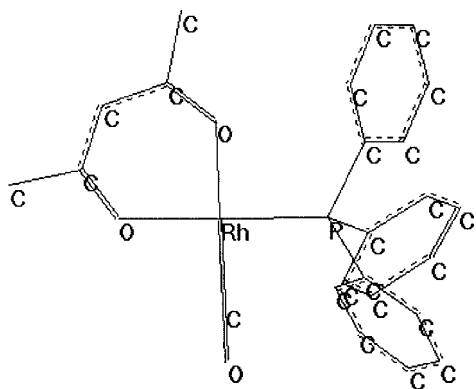


FIGURE 3. Rh(acetylacetonato)(CO)(PPh₃) structure imported from PCMODEL.

when parameters do not exist. MM⁺ force field parameters are given in ASCII text file formats, which are easily available for modification and additions.

The Rh(I) Carbonyl Phosphine force field was developed by the fitting of 15 known, square planar Rh(I) Carbonyl Phosphine structures.¹⁰ The X-ray crystallographic input data was read into PCMODEL¹¹ and converted to a Z-matrix mopac file, which was then imported in HyperChem (see Fig. 3 where Rh(acetylacetonato)(CO)(PPh₃) is given as an example).

A force field contains atom types and parameters that must be assigned to the molecule before a molecular mechanics calculation is performed. The atom types represent sets of atoms of the same element and define the classical environment of an atom together with its stereochemical properties. It is possible to distinguish between atoms by means of hybridization, formal charge on the atoms and immediate bonded neighbors.

New atom types were added to the existing MM⁺ force field and compiled to treat the new interactions incurred by the presence of the Rh(I) metal ion (Table I).

It was necessary to make some provision for the fact that there are two types of L—M—L angles (M = metal ion, L = ligand donor atom) in the complex, namely *cis* and *trans*. Above is called the *unique labeling problem*. A solution to the angle assignment problem was to make use of the valence force field method to define each ligand donor atom as a different atom type and to assign the appropriate ideal values to each of the individual angles (Fig. 4).

PARAMETERIZATION

There is a strong case for keeping parameterization as simple as possible.¹² Most molecular me-

chanics force fields already contain parameters for common organic functional groups. When modeling coordination compounds, it is generally assumed that the complexation of the ligand to a metal ion does not significantly alter the nature of the interactions within the ligand. The parameters used for modeling the ligand structure within a metal complex are therefore assumed to be transferable from organic force fields.¹³ The metal-dependent parameters are obtained by the same techniques, such as experimental data, that are used for the development of organic parameter sets. The performance of the initial set of parameters is tested by comparing calculated and experimental structures, together with their respective energies. If necessary, the initial parameters are then modified to minimize the errors in the calculated output.

Bond Stretching and Angle Bending Parameters

The valence force field method uses parameters for M—L stretches, M—L—X bends (X = any other atom type), and L—M—L bends.

"Ideal" bond lengths and "ideal" bond angles in the Rh(I) Carbonyl Phosphine force field were calculated by averaging the bond lengths and bond angles of the 15 mentioned X-ray structural data for a specific atom type.

Torsion Angle Parameters

The valence force field method requires the definition of parameters for M—L—X—X torsional interaction. These parameters are usually obtained by a trial-and-error fitting process in organic force fields.

The barriers of free rotation of the MM⁺ force field were copied to torsion angles in the Rh(I) Carbonyl Phosphine force field with the same valence geometry. The torsion terms around the Rh(I) metal center were omitted because the rotation barriers about Rh—L bonds are, in general, very low.¹⁴ This was done by setting the barriers of free rotation to zero.¹⁵

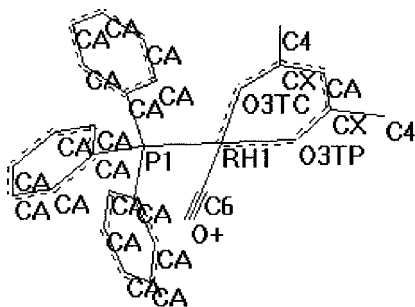
Nonbonding Parameters

For transition metals, van der Waals parameters have been roughly estimated by comparison with values that are used for the elements found in organic force fields. The valence force field method does not require the addition of nonbonded interactions with the metal ion, and it remains to be

TABLE I.
New Atom Type Entries.

Type	Mass	Remark
c2	12.000	4. C CSP ALKYNE, C=C=O''
c3	12.000	2. C CSP2 ALKENE
c4	12.000	1. C CSP3
c5	12.000	68. C sp3 CARBON bonded to fluoride
c6	12.000	74. C CARBONYL TO RHODIUM
c7	12.000	44. C sp3 CARBON bonded to sulphur
ca	12.000	50. C BENZENE
cx	12.000	76. C AROMATIC CARBON in bidentate ligands (6-ring)
cy	12.000	77. C AROMATIC CARBON in bidentate ligands (5-ring)
h	1.0079	5. H EXCEPT ON N/O
hn	1.008	23. H NH AMINE
n4	14.0067	82. N Co-ordinated NITROGEN; bonded to C; (6-ring)
n4tp	14.0067	87. N n4 trans to P
n4tc	14.0067	88. N n4 trans to CO
n5	14.0067	83. N Co-ordinated NITROGEN; bonded to C; (5-ring)
n5tp	14.0067	89. N n5 trans to P
n6	14.0067	80. N in bidentate ligand; bonded to O; (5-ring)
o ⁺	15.9994	75. O MONO POSITIVE OXYGEN; bonded to c6 (carbonyl)
o1	15.9994	7. O=O CARBONYL
o2	15.9994	6. O C—O—H, C—C—C''
o3	15.9994	78. O Co-ordinated OXYGEN; bonded to C; (6-ring)
o3tp	15.9994	90. O o3 trans to P
o3tc	15.9994	91. O o3 trans to CO
o5	15.9994	85. O Co-ordinated OXYGEN; bonded to C; (5-ring)
o5tp	15.9994	92. O o5 trans to P
o5tc	15.9994	93. O o5 trans to CO
o7	15.9994	86. O Co-ordinated OXYGEN; bonded to N; (5-ring)
o7tp	15.9994	94. O o7 trans to P
o7tc	15.9994	95. O o7 trans to CO
p1	30.994	84. P > P PHOSPHINE bonded to Rh
rh1	102.91	73. Rh RHODIUM (I)
s2	31.972	15. S—S SULPHIDE
s5	31.972	81. S Co-ordinated SULPHUR; bonded to C; (5-ring)
s7	31.972	79. S Co-ordinated SULPHUR; bonded to C; (6-ring)
s7tp	31.972	96. S s7 trans to P
s7tc	31.972	97. S s7 trans to CO

Numbers in remark column correspond to the atom type numbers in the MM⁺ force field.

**FIGURE 4.** Atom type selection of Rh(acetylacetonato)(CO)(PPh₃).

shown that the addition of metal ion nonbonded terms actually improves the performance of the force field.

Experimental force constants for any specific bond are clearly dependent on the environment and so are molecule specific. In molecular mechanics, however, generally applicable, and therefore, molecule independent force constants are needed. Force constants used in molecular mechanics are, therefore, not related to experimental observations, but are usually the result of extensive fittings.

The problem of force constants was also solved by copying force constants with similar chemical environments in the MM⁺ force field to the Rh(I) Carbonyl Phosphine force field where applicable. Force constants for the Rh—L bonds, Rh—L—X angles, L—Rh—L angles, Rh—L—X—X torsion angles, and each Rh···X nonbonding interaction that did not appear in the MM⁺ force field, were obtained by substituting the Rh(I) metal ion with a sp³-hybridized carbon,¹³ after which the routine of copying was continued. The Rh(I) Carbonyl Phosphine force field was, therefore, only an extension of the MM⁺ force field where the parameter sets contained all the bonding parameters of a purely organic force field together with parameters of a Rh(I) transition metal complex force field (see the Appendix).

It is important that the force field is reasonably balanced, i.e., no one component is so unrealistic that the other components must compensate for it to yield the net result in agreement with experimental data.

Energy Minimization and Geometry Optimization of the Structures in the Rhodium(I) Carbonyl Phosphine Force Field

The goal of performing a geometry optimization calculation is to characterize the potential energy minimum of an unknown Rh(I) structure, which is similar to that of the Rh(I) Carbonyl Phosphine structures. Before the Rh(I) Carbonyl Phosphine force field can be used to predict similar Rh(I) structures, the credibility of the parameters used in constructing it must be tested.

Geometry optimization was done using HyperChem on the series of 15 Rh(I) Carbonyl Phosphine structures by using a Newton-Raphson minimization procedure coded by Boyd.¹⁶

The structural properties of the minimized system were then compared with those of the X-ray crystallographic input data (Fig. 5) by means of a Turbo Pascal program. All strain energy minimized structures reproduced the observed X-ray structures to a tolerance of 0.02 Å in the Rh—L bond lengths and 3° in the Rh—L—X and L—Rh—L bond angles. The Rh(I) bond length and bond angle parameters outside the above criteria are listed below in Table II.

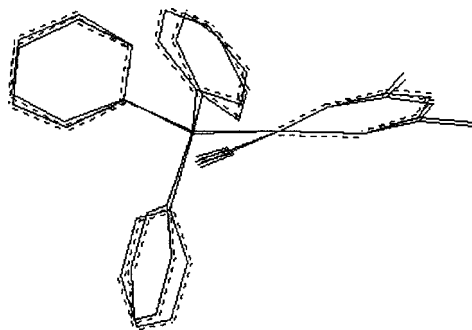


FIGURE 5. An overlay view of the minimized structure { } and the experimental X-ray determined structure { } of Rh(acetylacetonato)(CO)(PPh₃).

The Prediction of the Molecular Structure of Rh(1,3-diphenyl-1,3-propanedionato)(CO)(PPh₃)

The credibility of the parameters used in constructing the Rh(I) Carbonyl Phosphine force field was further tested by the prediction of the molecular structure of Rh(1,3-diphenyl-1,3-propanedionato)(CO)(PPh₃) (Fig. 6). The latter complex was synthesized, and its molecular structure determined by means of X-ray crystallography.¹⁷

The minimized Rh(1,3-diphenyl-1,3-propanedionato)(CO)(PPh₃) structure (Fig. 6a) reproduced the X-ray-determined Rh(1,3-diphenyl-1,3-propanedionato)(CO)(PPh₃)¹⁷ structure (Fig. 6b) also to a tolerance of 0.02 Å in the Rh—L bond lengths and 3° in the Rh—L—X and L—Rh—L bond angles (Table III).

The Computation of a Transition State during the Oxidative Addition of CH₃I to Rh(I) Carbonyl Phosphine Complexes

A promising extension in the area of applications of molecular mechanics is the calculation of the structures of short-lived intermediates.¹⁸ The problem here is that the calculated structures cannot be compared with experimental data and, therefore, rather large uncertainties have to be contended with.

The ligand "surface" in the space-filling mechanical models is representative of the points in space at which a repulsing interaction with other nonbonded atoms becomes important.¹⁹ The cone angle is a rough measure of the extent of this repulsing surface from the vantage point of a metal center.

TABLE II. **Rh(I) Bond Length and Bond Angle Parameters Outside the Given Tolerance Criteria Set for Reproducibility of the Minimized Structures.**

	X-ray Parameters	Computed Parameters	Difference
Rh(acetylacetonato)(CO)(PPh ₃) ^{10a} RH(2)—P1(6)	2.2372	2.2678	−0.030600
Rh(N-benzoyl-N-phenylhydroxylamino)(CO)(PPh ₃) ^{10b} RH(2)—P1(18) O7(3)—RH(2)—P1(18) RH(2)—P1(18)—CA(20)	2.2328 94.310 117.317	2.2670 97.564 114.107	−0.034200 −3.254000 3.210000
Rh(3-Benzylacetylacetonato)(CO)(PPh ₃) ^{10c} O3(1)—RH(2) RH(2)—P1(14)	2.0476 2.2420	2.0724 2.2667	−0.024800 −0.024700
Rh(2-Cyclohexylamino-1-cyclopentene-1-dithiocarboxylato)(CO)(PPh ₃) ^{10e} RH(2)—C6(12) RH(2)—P1(11)—CA(13) RH(2)—C6(12)—O ⁺ (41)	1.8294 117.288 171.503	1.7925 114.228 176.181	0.036900 3.060000 −4.678000
Rh(N-hydroxy-N-nitrosobenzenaminato)(CO)(PPh ₃) ^{10d} RH(2)—P1(6) RH(2)—P1(6)—CA(11)	2.2314 117.454	2.2667 113.994	−0.035300 3.460000
Rh(2-Amino-1-cyclopentene-1-dithiocarboxylato)(CO)(PPh ₃) ^{10f} RH(2)—C6(12)	1.8227	1.7976	0.025100
Rh(2-Methylamino-1-cyclopentene-1-dithiocarboxylato)(CO)(PPh ₃) ^{10g} N4(1)—RH(2) RH(2)—C6(10)	2.0877 1.8365	2.1150 1.7924	−0.027300 0.044100
Rh(8-Hydroxyquinolinato)(CO)(PPh ₃) ^{10h} N5(1)—RH(2) O5(3)—RH(2)—P1(10)	2.0981 91.312	2.1311 95.789	−0.033000 −4.477000
Rh(2-Carboxypyridinato)(CO)(PPh ₃) ¹⁰ⁱ RH(2)—O5(3) RH(2)—P1(10)—CA(14)	2.0666 121.164	2.0414 116.612	0.025200 4.552000
Rh(Thioacetylacetonato)(CO)(PPh ₃) ^{10j} RH(2)—O3(3) RH(2)—P1(6) RH(2)—C6(7)—O ⁺ (29)	2.0145 2.2961 180.000	2.0350 2.2664 175.358	−0.020500 0.029700 4.642000
Rh(1,1,1-Trifluoro-5,5-dimethylpentanedionato)(CO)(PPh ₃) ^{10l} RH(2)—O3(3)	2.0588	2.0370	0.021800
Rh(1,1,1-Trifluoro-5,5,5-trimethylpentanedionato)(CO)(PPh ₃) ¹⁰ⁿ RH(2)—O3(3) RH(2)—P1(9) RH(2)—C6(10)	2.0624 2.2366 1.7646	2.0346 2.2666 1.7931	0.027800 −0.030000 −0.028500
Rh(tropolonato)(CO)(PPh ₃) ^{10o} RH(2)—P1(11)	2.2328	2.2679	−0.035100

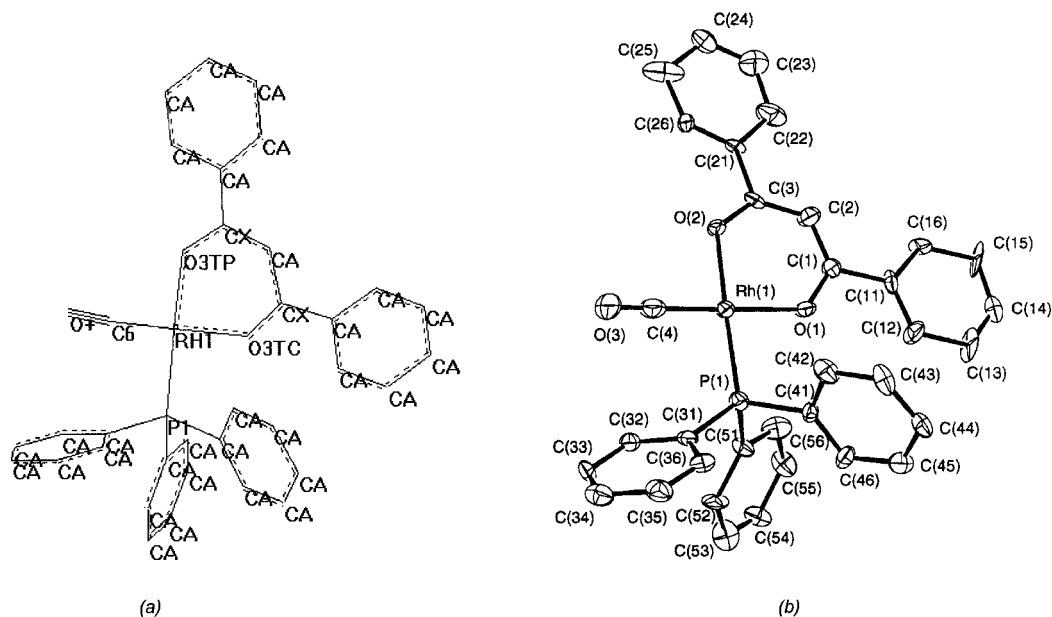


FIGURE 6. The structure of $\text{Rh}(1,3\text{-diphenyl-1,3-propanedionato})(\text{CO})(\text{PPh}_3)$ predicted by the $\text{Rh}(\text{I})$ Carbonyl Phosphine force field (a) vs. the X-ray determined structure (b).

The cone angle, the most widely accepted approach assessing ligand steric effects, is that suggested by Tolman.²⁰ A limitation of Tolman's approach is that it is difficult to decide on an appropriate cone angle for complex ligands, in which the van der Waals "surface" is highly irregular.

In molecular mechanics, steric effects are exerted through the van der Waals interactions between all atoms separated by at least two other atoms in the connectivity diagram for the molecule.²¹

An effective computational measure of ligand steric requirements must take into account that

TABLE III. Comparative Bond Lengths and Bond Angles of the Predicted and X-ray Determined Structures of $\text{Rh}(1,3\text{-diphenyl-1,3-propanedionato})(\text{CO})(\text{PPh}_3)$.

Predicted Structure of $\text{Rh}(1,3\text{-diphenyl-1,3-propanedionato})(\text{CO})(\text{PPh}_3)$		X-ray Determined Structure of $\text{Rh}(1,3\text{-diphenyl-1,3-propanedionato})(\text{CO})(\text{PPh}_3)$	
Rh1—P1	2.268 Å	Rh1—P1	2.237 Å
Rh1—O3TC	2.032 Å	Rh1—O1	2.038 Å
Rh1—O3TP	2.071 Å	Rh1—O2	2.081 Å
Rh1—C6	1.793 Å	Rh1—C4	1.812 Å
P1—Rh1—O3TC	92.4°	P1—Rh1—O1	87.7°
P1—Rh1—O3TP	176.0°	P1—Rh1—O2	175.2°
P1—Rh1—C6	89.4°	P1—Rh1—C4	91.1°
O3TC—Rh1—O3TP	87.1°	O1—Rh1—O2	88.5°
O3TC—Rh1—C6	176.5°	O1—Rh1—C4	175.3°
O3TC—Rh1—C6	90.8°	O2—Rh1—C4	92.9°
Rh1—P1—CA	114.0°	Rh1—P1—C31	119.8°
Rh1—P1—CA	115.5°	Rh1—P1—C51	113.4°
Rh1—P1—CA	111.9°	Rh1—P1—C51	110.7°
Rh1—O3TC—CX	131.3°	Rh1—O1—C1	127.5°
Rh1—O3TP—CX	129.3°	Rh1—O2—C3	125.1°
Rh1—C6—O ⁺	176.7°	Rh1—C4—O3	177.4°

steric forces are short range and repulsing.²² Secondly, it must permit evaluation of the steric effect of each ligand in an appropriate conformation; that is, one that is more or less typical of a ligand bound to a metal center. Given the predominantly non-bonded repulsing nature of the steric term, the focus should be not on the van der Waals interaction between ligand and metal, but only on the repulsing part of that interaction, for the lowest energy structure for the complex. The latter statement normally applies to metal complexes with a fully packed coordination sphere. However, in the present case, dealing with square planar complexes, interligand attraction are not expected to be the driving force of the resulting coordination.

The steric parameter should be a measure of the steric effect exerted by the ligand in its reactions with a metal center or that exerted when the ligand is bound to a metal undergoing a reaction. Individual ligands exert different effective steric demands from one reaction to the next as a result of the steric and electronic characteristics of the transition state.

The question as to whether the transition state during oxidative addition of CH_3I to Rh(I) Carbonyl Phosphine complexes is linear or three-centered was answered by the computation of the steric energy when CH_3I approaches the Rh(I) metal center.

The optimized structure of CH_3I was merged onto the optimized Rh(1,3-diphenyl-1,3-propanedionato)(CO)(PPh₃) structure. The coordinates of the Rh(I) metal atom were translated to the origin (0 0 0). The x and y coordinates of CH_3I remained constant at their respective origin positions after translating, whereas the z coordinate was varied perpendicular to the XY coordination plane of the Rh atom from 5 to 0.5 Å as the CH_3I molecule was approaching the Rh atom. After each variation of the z coordinates of the Carbon atom in CH_3I , the relative position of this molecule was optimized relative to the stationary Rh(1,3-diphenyl-1,3-propanedionato)(CO)(PPh₃) molecule (Fig. 7). A single point calculation was then performed on the entire system to determine the steric energy²³ in kcal.mol⁻¹ (Fig. 8).

The force field predicted only three approaches of the CH_3I to the Rh(I) metal center, two of which would lead to a concerted three-centered mechanism and one of which would lead to a $\text{S}_{\text{N}}2$ mechanism (Fig. 7).

The $\text{S}_{\text{N}}2$ approach was more stable, with lower steric energy values, than the concerted three-centered approach (Fig. 8), and was independent of the initial z coordinate translation of the carbon atom in CH_3I .

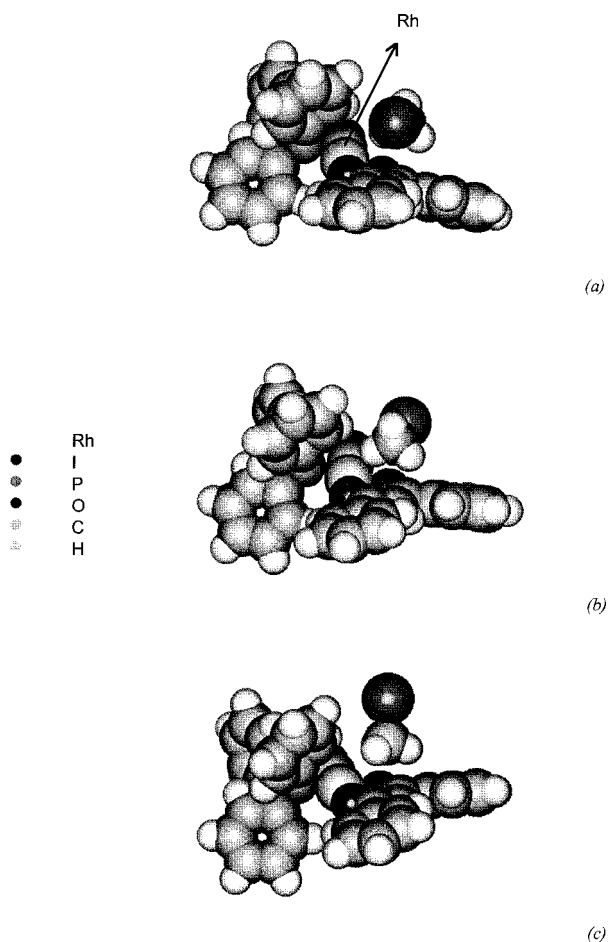


FIGURE 7. The three CH_3I approaches calculated by the force field. (a) and (b) approaches a concerted three-centered mechanism (c) approaches a linear $\text{S}_{\text{N}}2$ mechanism.

Discussion

THE PREDICTION OF Rh(1,3-DIPHENYL-1,3-PROPANEDIONATO)(CO)(PPh₃)

The excellent agreement between the observed and computed structures suggests that the set of parameters chosen for molecular mechanics calculation was appropriate (Fig. 5).

Comparing the predicted square planar Rh(1,3-diphenyl-1,3-propanedionato)(CO)(PPh₃) structure with the X-ray crystallographic structure (Fig. 6 and Table III) also suggests that the parameters chosen for constructing the force field were appropriate. The most conspicuous deviation in the bond length and bond angle criteria of 0.02 Å and 3° was the Rh1—P1 bond length. Considering X-ray crystallographic data of Rh(I) Carbonyl Phosphine com-

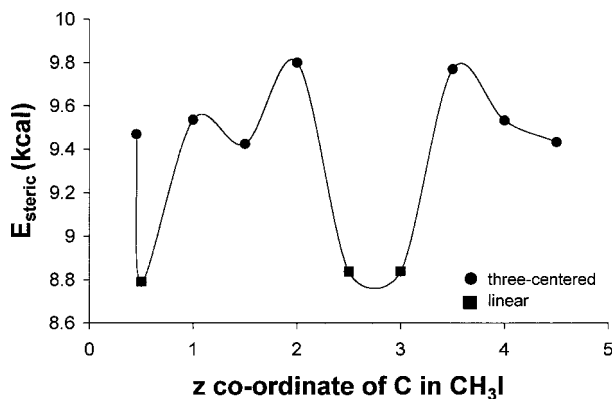


FIGURE 8. Plot of the steric energy obtained during optimization of CH_3I approaching $\text{Rh}(\text{1,3-diphenyl-1,3-propanedionato})(\text{CO})(\text{PPh}_3)$ vs. the initial z coordinate of the Carbon atom in CH_3I .

plexes, the estimated standard deviation of a $\text{Rh}-\text{P}$ bond is very small (0.001 \AA) relative to the estimated standard deviations of the other bond lengths and can, therefore, explain the relatively large deviation in the computed and X-ray determined $\text{Rh}-\text{P}$ bond lengths.

THE PREDICTION OF $\text{S}_{\text{N}}2$ MECHANISM

The computation of the transition state during the oxidative addition of CH_3I to $\text{Rh}(\text{1,3-}$

diphenyl-1,3-propanedionato)($\text{CO})(\text{PPh}_3)$ suggests a concerted three-centered transition state (Fig. 7a and b) and a linear transition state (Fig. 7c).

The steric energy calculated for the above was lower for the linear transition state than for the concerted three-centered transition state (Fig. 8). Oxidative addition of CH_3I to the $\text{Rh}(\text{I})$ Carbonyl Phosphine complexes will, therefore, rather occur via a $\text{S}_{\text{N}}2$ mechanism than a concerted three-centered mechanism. These results were also observed during *ab initio* calculations.²⁴

The second reaction path during oxidative addition of CH_3I to $\text{Rh}(\text{I})$ Carbonyl Phosphine complexes is an isomerization step (Fig. 1). A linear transition state will lead to *trans* addition of CH_3I and isomerization will, therefore, form a *cis* $\text{Rh}(\text{III})$ Carbonyl Phosphine isomer as final product.

The final *cis* isomer was also proven by means of a X-ray determined structure of $\text{Rh}(\text{III})(\text{N-hydroxy-N-nitrosobenzenaminato})(\text{CO})(\text{CH}_3)(\text{I})(\text{PPh}_3)$.²⁵ Unfortunately, only a few $\text{Rh}(\text{III})$ Carbonyl Phosphine structures have been isolated to date, and it was, therefore, not possible to develop an accurate $\text{Rh}(\text{III})$ Carbonyl Phosphine force field that could have been used to predict the most stable final isomer (*trans* $\text{Rh}(\text{III})$ Carbonyl Phosphine or *cis* $\text{Rh}(\text{III})$ Carbonyl Phosphine) formed during oxidative addition of CH_3I to $\text{Rh}(\text{I})$ Carbonyl Phosphine complexes.

Appendix

PARAMETER SETS OF THE $\text{Rh}(\text{I})$ CARBONYL PHOSPHINE FORCE FIELD

Bond Length Parameters

T1	T2	KS	L0	L1	DIPOLE	REMARK ⁹
n4tp	rh1	3.520	2.102	0.000	1.470	"Lamprecht, c4-n2, MM2"
n5tp	rh1	3.520	2.095	0.000	1.470	"Lamprecht, c4-n2, MM2"
o3tp	rh1	5.360	2.075	0.000	0.440	"Lamprecht, c4-o2, MM2"
o5tp	rh1	5.360	2.085	0.000	0.440	"Lamprecht, c4-o2, MM2"
o7tp	rh1	5.360	2.064	0.000	0.440	"Lamprecht, c4-o2, MM2"
rh1	c6	4.400	1.800	0.000	0.300	"Lamprecht, c4-co, MM2"
rh1	n4tc	3.520	2.019	0.000	1.470	"Lamprecht, c4-n2, MM2"
rh1	o3tc	5.360	2.037	0.000	0.440	"Lamprecht, c4-o2, MM2"
rh1	o5tc	5.360	2.047	0.000	0.440	"Lamprecht, c4-o2, MM2"
rh1	o7tc	5.360	2.035	0.000	0.440	"Lamprecht, c4-o2, MM2"
rh1	p1	2.910	2.256	0.000	0.830	"Lamprecht, c4-p, MM2"
rh1	s7tc	3.213	2.295	0.000	1.200	"Lamprecht, c4-s2, MM2"
s7tp	rh1	3.213	2.297	0.000	1.200	"Lamprecht, c4-s2, MM2"

Bond Angle Parameters

T1	T2	T3	KS	TYPE1	TYPE2	TYPE3	REMARK ⁹
n4tc	rh1	c6	0.820	177.2	111.1	109.8	"Lamprecht, co-c4-n2, MM2"
n4tc	rh1	p1	0.480	90.9	0.0	0.0	"Lamprecht, c4-c4-p, MM2"
n4tp	rh1	c6	0.820	95.3	111.1	109.8	"Lamprecht, co-c4-n2, MM2"
n4tp	rh1	o3tc	0.700	88.7	0.0	0.0	"Lamprecht, ca-c4-o2, c3→ca"
n4tp	rh1	p1	0.480	177.3	0.0	0.0	"Lamprecht, c4-c4-p, MM2"
n4tp	rh1	s7tc	0.580	93.7	108.0	114.8	"Lamprecht, n2-c4-s2, MM2"
n5tp	rh1	c6	0.820	96.6	111.1	109.8	"Lamprecht, co-c4-n2, MM2"
n5tp	rh1	o5tc	0.700	79.5	0.0	0.0	"Lamprecht, ca-c4-o2, c3→ca"
n5tp	rh1	p1	0.480	170.1	0.0	0.0	"Lamprecht, c4-c4-p, MM2"
o3tc	rh1	c6	0.700	177.1	0.0	0.0	"Lamprecht, co-c4-o2, MM2"
o3tc	rh1	p1	0.480	90.6	0.0	0.0	"Lamprecht, c4-c4-p, MM2"
o3tp	rh1	c6	0.700	92.0	0.0	0.0	"Lamprecht, co-c4-o2, MM2"
o3tp	rh1	o3tc	0.460	87.6	97.0	102.2	"Lamprecht, o2-c4-o2, MM2"
o3tp	rh1	p1	0.480	176.8	0.0	0.0	"Lamprecht, c4-c4-p, MM2"
o5tc	rh1	c6	0.700	175.1	0.0	0.0	"Lamprecht, co-c4-o2, MM2"
o5lc	rh1	p1	0.480	93.0	0.0	0.0	"Lamprecht, c4-c4-p, MM2"
o5tp	rh1	c6	0.700	98.0	0.0	0.0	"Lamprecht, co-c4-o2, MM2"
o5tp	rh1	o5tc	0.460	77.8	97.0	102.2	"Lamprecht, o2-c4-o2, MM2"
o5tp	rh1	o7tc	0.460	78.4	97.0	102.2	"Lamprecht, o2-c4-o2, MM2"
o5tp	rh1	p1	0.480	173.4	0.0	0.0	"Lamprecht, c4-c4-p, MM2"
o7tc	rh1	c6	0.700	174.7	0.0	0.0	"Lamprecht, co-c4-o2, MM2"
o7tc	rh1	p1	0.480	95.6	0.0	0.0	"Lamprecht, c4-c4-p, MM2"
o7tp	rh1	c6	0.700	98.1	0.0	0.0	"Lamprecht, co-c4-o2, MM2"
o7tp	rh1	o7tc	0.460	76.6	97.0	102.2	"Lamprecht, o2-c4-o2, MM2"
o7tp	rh1	p1	0.480	172.6	0.0	0.0	"Lamprecht, c4-o4-p, MM2"
p1	rh1	c6	0.480	88.8	0.0	0.0	"Lamprecht, c4-c4-p, MM2"
rh1	c6	o+	0.460	176.8	0.0	0.0	"Lamprecht, ca-p-ca, MM2"
rh1	n4tc	cx	0.630	133.8	0.0	0.0	"Lamprecht, c4-n2-ca, c3→ca"
rh1	n4tc	hn	0.440	120.3	0.0	0.0	"Lamprecht, c4-n2-hv, MM2"
rh1	n4tp	c4	0.760	117.2	0.0	0.0	"Lamprecht, c4-n2-c4, MM2"
rh1	n4tp	ca	0.630	121.7	0.0	0.0	"Lamprecht, c4-n2-ca, c3→ca"
rh1	n4tp	cx	0.630	126.8	0.0	0.0	"Lamprecht, c4-n2-ca, c3→ca"
rh1	n5tp	ca	0.630	112.3	0.0	0.0	"Lamprecht, c4-n2-ca, c3→ca"
rh1	n5tp	cx	0.630	127.1	0.0	0.0	"Lamprecht, c4-n2-ca, c3→ca"
rh1	o3tc	ca	0.770	129.3	0.0	0.0	"Lamprecht, c4-o2-ca, c3→ca"
rh1	o3tc	cx	0.770	129.8	0.0	0.0	"Lamprecht, c4-o2-ca, c3→ca"
rh1	o3tp	cx	0.770	125.7	0.0	0.0	"Lamprecht, c4-c2-ca, c3→ca"
rh1	o5tc	ca	0.770	144.4	0.0	0.0	"Lamprecht, c4-o2-ca, c3→ca"
rh1	o5tc	co	0.600	116.6	0.0	0.0	"Lamprecht, c4-o2-co, MM2"
rh1	o5tc	cy	0.770	116.1	0.0	0.0	"Lamprecht, c4-o2-ca, c3→ca"
rh1	o5tp	cy	0.770	113.5	0.0	0.0	"Lamprecht, c4-o2-ca, c3→ca"
rh1	o7tc	n6	0.770	111.1	0.0	0.0	"Lamprecht, c4-o2-ca, c3→ca"
rh1	o7tp	n6	0.770	115.4	0.0	0.0	"Lamprecht, c4-o2-ca, c3→ca"
rh1	p1	ca	0.480	114.6	0.0	0.0	"Lamprecht, c4-p-ca, c3→ca"
rh1	s7tc	ex	0.680	111.6	0.0	0.0	"Lamprecht, ca-sa-ca, c3→ca"
rh1	s7tp	cx	0.680	111.2	0.0	0.0	"Lamprecht, ca-sa-ca, c3→ca"
s7tc	rh1	c6	0.420	169.4	0.0	0.0	"Lamprecht, co-c4-s2, MM2"
s7tc	rh1	p1	0.480	86.6	0.0	0.0	"Lamprecht, c4-c4-p, MM2"
s7tp	rh1	c6	0.420	88.9	0.0	0.0	"Lamprecht, co-c4-s2, MM2"
s7tp	rh1	n4tc	0.580	91.3	108.0	114.8	"Lamprecht, n2-c4-s2, MM2"
s7tp	rh1	o3tc	0.700	91.9	0.0	0.0	"Lamprecht, ca-c4-o2, c3→ca"
s7tp	rh1	p1	0.480	177.9	0.0	0.0	"Lamprecht, c4-c4-p, MM2"

Torsion Parameters							
T1	T2	T3	T4	V1	V2	V3	REMARK ⁹
rh1	n4tc	cx	c4	-0.10	9.00	0.00	"Lamprecht, c4-ca-ca-c4, MM2"
rh1	n4tc	cx	ca	0.00	0.50	0.00	"Lamprecht, ca-ca-n2-c4, c3→ca"
rh1	n4tp	c4	c4	0.00	0.00	0.91	"Lamprecht, c4-c4-n2-c4, MM2"
rh1	n4tp	c4	h	0.00	0.00	-0.20	"Lamprecht, h-c4-n2-c4, MM2"
rh1	n4tp	ca	ca	0.00	0.50	0.00	"Lamprecht, ca-ca-n2-c4, c3→ca"
rh1	n4tp	cx	ca	0.00	0.50	0.00	"Lamprefat, ca-ca-n2-c4, c3→ca"
rh1	n4tp	cx	c4	-0.10	9.00	0.00	"Lamprecht, c4-ca-ca-c4, MM2"
rh1	n4tp	cx	h	0.00	9.00	0.00	"Lamprecht, c4-ca-ca-h, MM2"
rh1	n5tp	ca	ca	0.00	0.50	0.00	"Lamprebt, ca-ca-n2-c4, c3→ca"
rh1	n5tp	co	co	0.00	15.00	0.00	"Lamprecht, c4-ca-ca-co, c3→ca"
rh1	n5tp	cx	ca	0.00	0.50	0.00	"Lamprecht, ca-ca-n2-c4, c3→ca"
rh1	n5tp	cx	h	0.00	0.50	0.00	"Lamprecht, ca-ca-n2-c4, c3→ca"
rh1	o3tc	ca	ca	3.53	2.30	-3.53	"Lamprecht, ca-ca-o2-c4, c3→ca"
rh1	o3tc	cx	ca	3.53	2.30	-3.53	"Lamprecht, ca-ca-o2-c4, c3→ca"
rh1	o3tc	cx	c4	2.30	4.00	0.00	"Lamprecht, c4-ca-o2-c4, c3→ca"
rh1	o3tp	cx	ca	3.53	2.30	-3.53	"Lamprecht, ca-ca-o2-c4, c3→ca"
rh1	o3tp	cx	c4	2.30	4.00	0.00	"Lamprecht, c4-ca-o2-c4, c3→ca"
rh1	o3tp	cx	c5	2.30	4.00	0.00	"Lamprecht, c4-ca-o2-c4, c3→ca"
rh1	o5tc	ca	ca	3.53	2.30	-3.53	"Lamprecht, ca-ca-o2-c4, c3→ca"
rh1	o5tc	co	ca	0.00	11.10	0.00	"Lamprecht, c4-ca-co-ca, c3→ca"
rh1	o5tc	co	o1	2.75	15.00	0.00	"Lamprecht, c4-ca-co-ol, c3→ca"
rh1	o5tc	cy	cy	3.53	2.30	-3.53	"Lamprecht, ca-ca-o2-c4, c3→ca"
rh1	o5tc	cy	c3	3.53	2.30	-3.53	"Lamprecht, c3-ca-o2-c4, c3→ca"
rh1	o5tp	cy	n6	3.53	2.30	-3.53	"Lamprecht, ca-ca-o2-c4, c3→ca"
rh1	o5tp	cy	ca	3.53	2.30	-3.53	"Lamprecht, ca-ca-o2-c4, c3→ca"
rh1	o5tp	cy	cy	3.53	2.30	-3.53	"Lamprecht, ca-ca-o2-c4, c3→ca"
rh1	o5tp	cy	c3	3.53	2.30	-3.53	"Lamprecht, c3-ca-o2-c4, c3→ca"
rh1	o7tc	n6	cy	3.53	2.30	-3.53	"Lamprecht, ca-ca-o2-c4, c3→ca"
rh1	o7tc	n6	ca	3.53	2.30	-3.53	"Lamprecht, ca-ca-o2-c4, c3→ca"
rh1	o7tc	n6	n6	0.00	10.00	0.00	"Lamprecht, ca-ca-na-na, c3→ca"
rh1	o7tp	n6	n6	0.00	10.00	0.00	"Lamprecht, ca-ca-na-na, c3→ca"
rh1	p1	ca	ca	0.00	0.00	0.40	"Lamprecht, ca-ca-p-c4, c3→ca"
rh1	s7tc	cx	s2	0.00	15.00	2.60	"Lamprecht, ca-ca-ca-sa, c3→ca"
rh1	s7tc	cx	ca	0.00	1.70	0.40	"Lamprecht, ca-ca-sa-ca, c3→ca"
rh1	s7tp	cx	ca	0.00	1.70	0.40	"Lamprecht, ca-ca-sa-ca, c3→ca"
rh1	s7tp	cx	s2	0.00	15.00	2.60	"Lamprecht, ca-ca-ca-sa, c3→ca"
rh1	s7tp	cx	c4	-0.10	9.00	0.00	"Lamprecht, c4-ca-ca-c4, MM2"

Out-of-Plane Bending Parameters				Nonbonded Parameters			
C	A	COPB	REMARK ⁹	TYPE	RSTAR	EPS	REMARK ⁹
ca	p1	0.500	"Lamprecht, (ca p), c3→ca"	rh1	1.9000	0.0440	"Lamprecht, c4, MM2"
ca	cx	0.050	"Lamprecht, (ca ca), MM2"	o3tc	1.7400	0.0500	"Lamprecht, o2, MM2"
ca	cy	0.050	"Lamprecht, (ca ca), MM2"	o5tp	1.7400	0.0500	"Lamprecht, o2, MM2"
ca	n6	0.050	"Lamprecht, (ca n2), c3→ca"	o7tc	1.7400	0.0500	"Lamprecht, o2, MM2"
ca	o5tc	0.050	"Lamprecht, (ca o2), c3→ca"	n6	1.8200	0.0550	"Lamprecht, n2, MM2"
ca	n5tp	0.050	"Lamprecht, (ca n2), c3→ca"	cy	1.9400	0.0440	"Lamprecht, ca, MM2"
co	o5tc	0.800	"Lamprecht, (co o2), MM2"	n4tp	1.8200	0.0550	"Lamprecht, n2, MM2"
ca	o3tc	0.050	"Lamprecht, (ca o2), c3→ca"	s7tc	2.1100	0.2020	"Lamprecht, s2, MM2"
ca	n4tp	0.050	"Lamprecht, (ca n2), c3→ca"	c7	1.9000	0.0440	"Lamprecht, c4, MM2"
c3	cy	0.050	"Lamprecht, (c3 ca), c3→ca"	o7tp	1.7400	0.0500	"Lamprecht, o2, MM2"
				s7tp	2.1100	0.2020	"Lamprecht, s2, MM2"

n4tc	1.8200	0.0550	"Lamprecht, n2, MM2"
n5tp	1.8200	0.0550	"Lamprecht, n2, MM2"
o5tc	1.7400	0.0500	"Lamprecht, o2, MM2"
c5	1.9000	0.0440	"Lamprecht, c4, MM2"

References

1. Foster, D. *Adv Organomet Chem* 1979, 17, 255.
2. Foster, D.; Singleton, T. D. *J Mol Catal* 1982, 17, 299.
3. Lamprecht, G. J.; Beetge, J. H. S. *Afr J Chem* 1987, 40, 131.
4. van Zyl, G. J.; Lamprecht, G. J.; Leipoldt, J. G. *Inorg Chim Acta* 1986, 122, 75.
5. Leipoldt, J. G.; Basson, S. S.; Botha, L. J. *Inorg Chim Acta* 1990, 168, 215.
6. Venter, J. A.; Leipoldt, J. G.; van Eldik, R. *Inorg Chem* 1991, 30, 2207.
7. van Zyl, G. J.; Lamprecht, G. J.; Leipoldt, J. G.; Swaddle, T. W. *Inorg Chim Acta* 1988, 143, 223.
8. HyperChem (TM), Getting Started, Molecular Visualization and Simulation; Hypercube, Inc., 1994.
9. Allinger, N. L. *J Am Chem Soc* 1977, 99, 8127.
10. (a) Leipoldt, J. G.; Basson, S. S.; Bok, L. D. C.; Gerber, T. I. A. *Inorg Chim Acta* 1978, 26, L35; (b) Leipoldt, J. G.; Grobler, E. C. *Inorg Chim Acta* 1982, 60, 141; (c) Roodt, A.; Leipoldt, J. G.; Swarts, J. C.; Steyn, G. J. *J. Acta Crystallogr* 1992, C48, 547; (d) Basson, S. S.; Leipoldt, J. G.; Roodt, A.; Venter, J. A. *Inorg Chim Acta* 1986, 118, L45; (e) Steyn, G. J. J.; Roodt, A., to appear; (f) Steyn, G. J. J.; Roodt, A.; Poletaeva, I.; Varshavsky, Y. S. *J Organomet Chem* 1997, 536, 197; (g) Steyn, G. J. J.; Roodt, A.; Leipoldt, J. G. *Inorg Chem* 1992, 31, 3477; (h) Leipoldt, J. G.; Basson, S. S.; Dennis, C. R. *Inorg Chim Acta* 1981, 50, 121; (i) Leipoldt, J. G.; Lamprecht, G. J.; Graham, D. E. *Inorg Chim Acta* 1985, 101, 123; (j) Botha, L. J.; Basson, S. S.; Leipoldt, J. G. *Inorg Chim Acta* 1987, 126, 25; (k) Leipoldt, J. G.; Basson, S. S.; Grobler, E. C.; Roodt, A. *Inorg Chim Acta* 1985, 99, 13; (l) Leipoldt, J. G.; Basson, S. S.; Nel, J. T. *Inorg Chim Acta* 1983, 74, 85; (m) Steynberg, E. C.; Lamprecht, G. J.; Leipoldt, J. G. *Inorg Chim Acta* 1987, 133, 33; (n) Leipoldt, J. G.; Basson, S. S. *Inorg Chim Acta* 1986, 117, L3; (o) Leipoldt, J. G.; Lok, L. D. C.; Basson, S. S.; Meyer, H. *Inorg Chim Acta* 1980, 42, 105.
11. PCMODEL, Molecular modelling software, IBM RS/6000; Serena Software: Bloomington, IN, 1990.
12. Bernhardt, P. V.; Comba, P. *Inorg Chem* 1992, 31, 2638.
13. Hay, B. P. *Co-ord Chem Rev* 1993, 126, 177.
14. Buckingham, D. A.; Sargeson, A. M. *Top Stereochem* 1971, 6, 219.
15. Boeyens, J. C. A.; Cotton, F. A.; Han, S. J. *Inorg Chem* 1985, 24, 1750.
16. Boyd, R. H. *J Chem Phys* 1968, 49, 2574.
17. Lamprecht, D.; Lamprecht, G. J.; Botha, J. M.; Umakoshi, K.; Sasaki, Y. *Acta Crystallogr* 1997, C53, 1403.
18. Comba, P. *Co-ord Chem Rev* 1993, 123, 1.
19. Caffery, M. L.; Brown, T. L. *Inorg Chem* 1991, 30, 3907.
20. Tolman, C. A. *Chem Rev* 1977, 77, 313.
21. Brown, T. L. *Inorg Chem* 1992, 31, 1286.
22. Lee, K. J.; Brown, T. L. *Inorg Chem* 1992, 31, 289.
23. HyperChem (TM), Reference, Molecular Visualization and Simulation; Hypercube, Inc., 1994.
24. Griffin, T. R.; Cook, D. B.; Haynes, A.; Pearson, J. M.; Monti, D.; Morris, G. E. *J Am Chem Soc* 1996, 118, 3029.
25. Basson, S. S.; Leipoldt, J. G.; Roodt, A.; Venter, J. A. *Inorg Chim Acta* 1987, 128, 31.